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A Study of Samples of Well Water Collected from Selected Areas in California to Determine the Presence of DBCP and Certain Other Pesticide Residues

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Liquid 1,2-dibromo-3-chloropropane (DBCP) was used as a soil nematicide in California from the late 1950's through early August 1977 when registration for use in California was cancelled because of its identified potential as a carcinogen in test animals and as a testicular toxin in test animals and man. Usage elsewhere in the United States and the world continued beyond that time. The major usage in California had been in the sandy soil areas of the east side of the San Joaquin Valley, the valleys of Ventura County, and the irrigated desert areas of Riverside County. There had been limited use in the central coastal valleys.

The primary crops that had been treated included grapes, citrus, peaches, tomatoes, cotton, almonds, and other nut and stone fruit crops. Dosage of DBCP ranged from about 20 to 80 pounds per acre. Application frequency ranged from annual to about once in 5 years with a median of once each 3 years.

Most applications were made in the fall, but some were made each month of the year. Accurate records are not available, but usage in California was considered to have increased at a sharp rate shortly after 1960 and then maintained at about 3,000,000 pounds per year until registration was cancelled.

Applications were made by the addition of DBCP at the rate of about 30 ppm in flowing irrigation water entering a field, or by injection of concentrated DBCP into the soil using tractor-mounted shank injection equipment.

Earlier studies had indicated that very little DBCP was found in the first foot of topsoil 2 to 3 years after application.

The authors tested 32 fields that had been treated with DBCP 2 to 4 years before, and found that the surface of the topsoil contained about 2 to 5 ppb of DBCP. The authors also found from other studies that during the first month after treatment, surface soil may contain up to 1 ppm of DBCP, with considerably higher amounts found down to the 8 inch level.

It had been thought by some that most DBCP volatilized during the first month after treatment. Studies by the authors have shown that air levels of DBCP 4 feet above shank-injection-treated soil rarely exceed 1 ppb beyond 1 day post treatment. Even during

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water-run treatments in which no attempt was made to reduce volatility, air concentrations 4 feet above the surface did not exceed 300 ppb for more than a few hours during application.

Contact with various soil constituents may contribute to breakdown of DBCP into other chemicals; however, it now appears that, in time, some DBCP moves downward through the soil and into water.

In February and March 1979, water samples collected by the Central Valley Regional Water Quality Control Board (CVRWQCB) from several wells near Lathrop (near Stockton) were found to contain from 4 to 68 ppb of DBCP. Since those wells were not far from a pesticide dump site of the Occidental Chemical Company, which had previously manufactured DBCP, it was assumed that this was the source of the contamination. Use of water from these wells ceased shortly thereafter when clean water was piped into the area.

Between April 4 and May 2, 1979, water from 1 well in Butte County and from 9 wells in Stanislaus County were sampled by the CVRWQCB and analyzed by a commercial laboratory, and 2 samples from wells in Stanislaus County were found to contain residues of DBCP. At that time, the Department of Food and Agriculture was also asked to analyze the same samples and to gather and analyze additional samples from Stanislaus County wells for possible DBCP contamination. When some of these wells were found, after analysis of the water by the department's laboratory, to contain low levels of DBCP, the survey was expanded.

MATERIALS AND METHODS

The expanded survey included wells (primarily rural) of various depths in the counties of Yolo, San Joaquin, Stanislaus, Merced, Fresno, Tulare, Ventura, and Riverside. Sampling focused primarily on selected areas in several counties where DBCP had previously been used in plantings of grapes, peaches, citrus, almonds, and tomatoes.

Samples were collected from the running water from a well after the pump had been operating at least 1 minute. The person sampling put on new disposable polyethylene gloves and opened a new 16-ounce glass jar with a metal lid that had been closed over aluminum foil. After the jar had been filled to the top, the aluminum foil was put back in place, the screw cap was closed, and the gloves were disposed of. The water samples were kept cool, but were not frozen. Analysis was accomplished within 4 days of sample collection.

The following number of the water samples were also tested for the presence of other pesticides: ethylene dibromide (EDB) and 1,3-dichloropropene (1,3-D), 72 each; toxaphene, chlordane, lindane, aldrin, heptachlor, heptachlor epoxide, DDD, DDT, DDE, dicofol, tetradifon, methoxychlor, endosulfan I, endosulfan II, and endosulfan III, 87 each; and pentachlorophenol, 15.

Samples of milk produced at 10 daires were collected at farm milk-producing dairies in areas of the State where DBCP had previously been used.

The presence of DBCP, EDB, and 1,3-D was determined by codistillation of the DBCP, EDB, and 1,3-D with ethyl acetate. Other chlorinated compounds of interest were extracted by partitioning into organic solvent, and were determined by electron capture gas chromatography. Pentachlorophenol was analyzed by standard EPA methods.

Water samples were tested for the presence of DBCP and EDB, each with a method giving a minimum detection limit (MDL) of 100 ppt, and 1,3-D with a MDL of 1 ppb.

Water samples were tested for the presence of organochlorine compounds with the following minimum detection levels:

Lindane	0.1 ppb	Chlordane	20.0 ppb
Heptachlor	0.1 ppb	Toxaphene	20.0 ppb
Heptachlor epoxide	0.1 ppb	Methyoxychlor	4.0 ppb
DDD	0.1 ppb	Tetradifon	0.1 ppb
DDT	1.4 ppb	Endosulfan I	0.1 ppb
DDE	0.3 ppb	Endosulfan II	0.1 ppb
Dicofol	5.0 ppb	Endosulfan III	5.0 ppb
Pentachlorophenol	1.0 ppb		

For DBCP, EDB, and 1,3-D, a 150 mL aliquot of the water sample was transferred into a 500-mL boiling flask. A known quantity of ethyl acetate, typically 10 mL, was added. The sample was slowly distilled until all of the ethyl acetate and several mLs of water were collected in a Barrett trap. The trapped water was then drained off and discarded. The ethyl acetate was collected in a glass stoppered test tube, shaken with granular sodium sulfate, and analyzed by electron capture gas chromatography for the compound(s) of interest.

The distillation apparatus consisted of a heating mantle with a variable input transformer, the 500-mL boiling flask, a 20 mL Barrett trap, and a 300 mm Allihn condenser with chilled water.

The DBCP was confirmed in two different ways. Whenever possible, the samples showing positive gas chromatographic results were subjected to mass spectrometry for confirmation. Secondly, a series of samples containing a blank distilled water sample plus several samples which had tested positive for DBCP by gas chromatography (0.1 to 10.0 ppb) were sent out on a blind collaborative study to 5 other reputable laboratories with expertise in pesticide residue chemistry and/or water analysis. The other laboratories ran the samples for DBCP by 3 different extraction methods: distillation, partition into hexane, and partition into benzene; and by gas chromatography; and in 2 cases, by mass spectrometry as well.

All collaborating laboratories produced similar qualitative and quantitative results.

RESULTS

The analytical results for DBCP are given in Tables 1 through 3. Several samples found to contain DBCP using gas chromatography (GC) were also analyzed by mass spectrometry, with all giving positive results. The GC results were divided into 3 general groups: (1) For Yolo County in the Sacramento Valley, all samples were negative even though all wells were less than 100 feet deep. This might be related to the heavy clay type soil. The other areas tested in the State had more sandy soil. (2) The Ventura and Riverside County (Southern California) samples constituted another group of primarily negative samples taken from deeper wells; and (3) The third group of samples--those from the east side of the San Joaquin Valley--constituted most of the contaminated wells, with about half the wells tested showing residues of DBCP, with an average value of 5.0 ppb present in the contaminated wells. It appeared that the wells less than 100 feet deep were more likely to be contaminated.

Municipal water supplies of 30 towns or cities were tested, and 4 were found contaminated. The municipal water supplies in the geographic areas where there was contamination of rural water supplies were also almost entirely from wells. These wells differed from rural wells in 3 respects. Generally, they were (1) usually much deeper--about 300 feet, (2) in the urban area not near groves and vineyards, and (3) considered to be so tightly sealed at the top to prevent surface contamination that water treatment for excess bacteria is rarely necessary.

The results of the tests on milk were all negative.

The results of the tests for other pesticide residues were all negative.

DISCUSSION

In Ventura County, only one well was found to be contaminated with DBCP. This was on the citrus ranch where two 10-acre experimental applications of DBCP had been made in 1978. In all other areas of the State that were tested, no known DBCP applications had been made for at least two years. It is therefore possible that DBCP residues in water may persist for a number of years.

Dermal exposure to DBCP residues in irrigation water is not anticipated to result in any significant adverse health effects. The DBCP concentrations are not considered to be high enough to constitute any significant adverse health hazard if consumed by domestic animals.

The drinking of contaminated water by man is of concern. The levels found are probably sufficiently low to have no adverse

TABLE 1

Summary of analyses for levels of DBCP found in wells in California in May 1979.

Area	High Positive Sample (ppb)	Low Positive Sample (ppb)	Average of Positive Wells (ppb)	Number of Positive Wells	Total Number of Wells
Sacramento Valley	0	0	0	0	11
East side of the San Joaquin Valley	39.2	0.1	5.0	59	119
Ventura and Coachella Valleys	1.4	0.1	0.5	7	45
Municipal water supplies	9.5	0.1	1.4	14	61*
Farm labor camps	6.8	1.0	4.0	6	16
Milk producing dairies	16.4	0.1	5.0	4	10
			Total	90	262

* Most municipal samples were for water from more than one well.

TABLE 2

Range of levels of DBCP found in selected wells tested in California in May 1979:

DBCP Residue Levels (ppb)	Domestic	Irrigation	Domestic & Irrigation	Unknown	Totals
None detected	121	34	11	2	168
0.1 - 0.9	24	9	1	-	34
1.0 - 9.9	36	14	-	-	50
10.0 - 19.9	2	5	1	-	8
> 20.0	1	1	-	-	2
Totals	184	63	13	2	262

61 municipal wells, 16 farm labor camp wells, and 10 milk producing dairy water wells are included under "domestic wells."

Of the 61 municipal wells, 43 had no DBCP detected; 10 were found to have between 0.1 ppb and 0.9 ppb; and 8 were found to have between 1.0 ppb and 9.9 ppb.

Of the 16 farm labor camp wells, 10 had no DBCP detected, and 6 were found to have between 1.0 ppb and 9.9 ppb.

Of the 10 milk producing dairy wells, 6 had no DBCP detected, 1 was found to have between 0.1 ppb and 0.9 ppb, and 3 were found to have between 1.0 ppb and 9.9 ppb.

TABLE 3

SAMPLED WELLS IN CALIFORNIA THAT TESTED POSITIVE FOR DBCP
BY TYPE OF WELL BY COUNTY

County	Well Type	Residue (ppb)	County	Well Type	Residue (ppb)
San Joaquin	Domestic	0.9	Fresno	Irrigation	39
San Joaquin	Domestic	3.7	Fresno	Irrigation	15
Stanislaus	Domestic	2.1	Tulare	Irrigation	3.5
Stanislaus	Domestic	3.6	Tulare	Irrigation	8.1
Stanislaus	Domestic	6.6	Tulare	Irrigation	5.4
Stanislaus	Domestic	7.8	Tulare	Irrigation	3.8
Stanislaus	Domestic	0.5	Tulare	Irrigation	1.5
Stanislaus	Domestic	0.3	Tulare	Irrigation	4.3
Stanislaus	Domestic	0.1	Ventura	Irrigation	1.4
Stanislaus	Domestic	1.0	Riverside	Irrigation	0.4
Stanislaus	Domestic	1.5	Riverside	Irrigation	0.1
Stanislaus	Domestic	0.5	Riverside	Irrigation	0.1
Stanislaus	Domestic	4.8	Stanislaus	Irrigation Canal	0.1
Stanislaus	Domestic	17	Stanislaus	Irrigation	1.4
Stanislaus	Domestic	18	Stanislaus	Irrigation	1.1
Stanislaus	Domestic	9.4	Stanislaus	Irrigation	1.6
Stanislaus	Domestic	1.3	Stanislaus	Irrigation	1.6
Stanislaus	Domestic	1.0	Stanislaus	Irrigation	4.6
Stanislaus	Domestic	0.1	Stanislaus	Irrigation	10
Stanislaus	Domestic	8.6	Stanislaus	Irrigation	11
Stanislaus	Domestic	5.5	Stanislaus	Irrigation	11
Stanislaus	Domestic	0.5	San Joaquin	Labor Camp	6.8
Stanislaus	Domestic	4.2	San Joaquin	Labor Camp	5.1
Merced	Domestic	1.5	Merced	Labor Camp	1.0
Merced	Domestic	4.3	Fresno	Labor Camp	4.6
Merced	Domestic	0.8	Tulare	Labor Camp	4.2
Merced	Domestic	1.0	Riverside	Labor Camp	2.5
Merced	Domestic	0.3	San Joaquin	Dairy	1.5
Fresno	Domestic	2.1	Fresno	Dairy	1.9
Fresno	Domestic	1.1	Tulare	Dairy	0.1
Fresno	Domestic	1.3	Tulare	Dairy	16
Fresno	Domestic	0.6	Merced	Municipal	0.6
Fresno	Domestic	1.3	Merced	Municipal	0.1
Fresno	Domestic	0.9	Merced	Municipal	1.1
Fresno	Domestic	4.0	Merced	Municipal	0.4
Fresno	Domestic	23	Merced	Municipal	0.1
Tulare	Domestic	0.2	Merced	Municipal	1.6
Tulare	Domestic	0.8	Merced	Municipal	0.5
Tulare	Domestic	5.3	Merced	Municipal	0.2
Riverside	Domestic	0.9	Merced	Municipal	0.3
Riverside	Domestic	0.3	Fresno	Municipal	0.1
Fresno	Domestic & Irrigation	14	Fresno	Municipal	0.4
Riverside	Domestic & Irrigation	0.3	Fresno	Municipal	1.1
San Joaquin	Irrigation	0.2	Fresno	Municipal	2.1
San Joaquin	Irrigation	3.9	Fresno	Municipal	1.1
San Joaquin	Irrigation	0.3	Tulare	Municipal	0.4
San Joaquin	Irrigation	14	Tulare	Municipal	2.3
Merced	Irrigation	0.2	Tulare	Municipal	9.5
Merced	Irrigation	0.4	Tulare	Municipal	2.4
Merced	Irrigation	0.4	Merced	Unknown	6.0

effect on testicular function, but there is concern about the carcinogenic hazard to man.

The California Department of Health Services has set a temporary action level at 1 ppb, and has recommended that water above this level not be consumed by humans. The U.S. Environmental Protection Agency has under consideration a recommendation for a permanent ceiling level of 50 ppt.

After the study herein reported was concluded, the California Department of Health Services tested water from large numbers of municipal wells, and found additional large numbers of contaminated wells in the same general geographic areas.

CONCLUSIONS

The precise mechanism whereby DBCP residues contaminate water supplies is not known. It is, therefore, unlikely that DBCP can be kept out of ground water supplies if current application technology is followed. For this reason, and considering the widespread nature of contamination of well water, it is not likely that further agricultural use of DBCP should be authorized.